

Bits of Christ: An Archaeochemical Pigment Analysis of a Medieval Sculpture of Christ

An Honors Thesis (HONR 499)

by

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ABSTRACT

The Middle Ages lasted from 500 AD through 1500. Fascination with Medieval religious depictions, advancements in science and exploration during the Age of Discovery, and the evolution of artistic techniques during the Renaissance continue to interest scholars and artists today. Much is known about major trends of these evolutions in science, art, and religion through the diligent qualitative work of artists, historians, and scholars. What if this qualitative analysis could be performed in tandem with quantitative analysis? How much more could we understand about historical trends and Medieval Religious art in particular? Advancements in spectroscopic analytical techniques within the field of chemistry, for example, can confirm the types of pigments used on art pieces. These known pigments can then be connected to historic periods of artistic use, thus confirming or identifying a date range in which an artistic piece would have been created. I demonstrate the value of this type of interdisciplinary research through the chemical, archaeological, and historical analysis of the Medieval *Christ* sculpture currently housed in the David Owsley Museum of Art at Ball State University.

ACKNOWLEDGEMENTS

I would like to thank Dr. Patricia Lang for the immense amount of expertise, patience, and assistance that she has provided to me throughout this daunting two year process.

I would like to thank Carl Schaffer and the countless individuals at the David Owsley Museum of Art for allowing me access to the *Christ* sculpture and providing me with a vast array of artistic and historical knowledge.

I would like to thank Dean James Ruebel for embracing this thesis proposal and making my time as a Ball State Cardinal possible.

I would like to thank my father Gary, my mother Janice, and my siblings for providing constant encouragement throughout this task.

AUTHOR'S STATEMENT

The supernatural effect on daily life, religious idolatry, and religion have been at the center of artistic expression since the earliest human civilizations left chiseled etchings in stone slabs, hand smeared and mouth blown pigments on cave walls, and hand carved figures. Other forms of artistic mediums of worship include pottery, dance, music, paintings, and sculpture. These expressions of faith offer lenses into past societies and cultures. Artifacts from the hand carved pre-historic Venus of Willendorf figure, to the Great Pyramids of Egypt, to the minor lithics scatter of a paleo-Indian tribe in the Midwestern United States, every artifact countless stories to tell. The key to unlocking these stories is an interdisciplinary approach that combines knowledge and techniques from multiple fields, including archaeology, art history, and chemistry. I applied this interdisciplinary approach to confirm the believed 1225-1250 date of the crucifix titled *Christ* currently displayed at the David Owsley Museum of Art.

In my honors thesis, titled "Bits of Christ," I performed a two part research scheme comprised of both independent and archival research elements. The objective of my thesis was to quantitatively understand the qualitative information known about the medieval crucifix. I carried out independent molecular and elemental spectroscopic analysis of pigment samples removed from the crucifix. This analysis was performed with infrared spectroscopy, scanning electron microscope-energy dispersive spectroscopy, and close examination of paint chips with a high resolution microscope.

These analytical methods helped me identify the molecular and atomic structures present in each pigment. These compositions are characteristic of certain pigments. An example from this analysis was the identification of mercury(II) sulfide which is more commonly known as cinnabar. While art historians could hypothesize that this pigment was cinnabar through examination of visual characteristics, chemical identification can conclusively determine that it is

indeed cinnabar. This knowledge then ties the artifact to the specific time period in which cinnabar was commonly used. This component comprised the independent research portion of my thesis and effectively utilized my understanding of spectroscopic analytical techniques.

I also performed cultural and historical archival research over the Romanesque and Gothic periods of Medieval art. Information from this research helped place my independent chemical research in its proper historic and cultural context. Archival research bridged the disciplines of art history, medieval history, archaeology, and archaeometry.

My research focused on the corpus figure titled *Christ* which is part of the current collection on display at the David Owsley Museum of Art. This piece is an oak sculpture in the round with pigment, cloth, and metal mediums. It is believed to originate from Northern Catalan region of Spain during the 25 year period prior to 1250. The description on the name plate states:

*“Christ 1225-1250
Spanish
Catalan*

Prominent ribs, gory rivulets of blood and drooping “lifeless” head characterize this sculpture of Christ and emphasize his physical suffering during the crucifixion. Before the 13th century when this was made Christ was frequently shown as a king, standing in front of the cross with his arms outstretched. Later, artists usually depicted the crucifixion itself. In the 13th century, Christians practiced devotions that centered on visualizing the death of Christ. Sculptures like this would have enhanced their meditations.”¹³

The proposed date of this sculpture places it in both the Romanesque Period and the Gothic Period of Medieval art. The Romanesque period of medieval art occurred during the early thirteenth century. Romanesque Christian art often focused on the majesty of Christ. Crucifixes typically depicted an alive Christ nailed to brightly colored crucifixes.¹⁴ Even during the moments of death on the cross, Christ was filled with calm and serenity. His composure on the cross, in Romanesque sculpture, depicts strength, glory, and an elevated state above man.

Romanesque crucifix depictions have characteristic physical traits. Christ is carved with a full straight body. Arms are extended at a 90 degree angle and strongly support the weight of Christ's body on the cross. Fingers are curled over the nails in his palms to hide the grisly wounds. His head is shown with chin held high, eyes open,¹⁵ and hair pulled back under a crown of gold or thorns. Romanesque crucifixion depictions typically have four nails, one in each hand and foot, allowing the body of Christ to be presented straight on to the viewer in the sturdy form of a cross. In these depictions Christ is also presented fully robed in beautiful and valuable garbs.¹⁶ The aims of Romanesque religious art seems to be the portrayal the majesty of Christ even at his moment of death. Romanesque iconography elevated Christ to a divine pedestal.¹⁷

The Gothic period of art stood in drastic contrast to the Romanesque Period. Christ was typically depicted as dead on the cross. His body was often twisted at the torso to allow a single nail to be driven into both feet holding them against the cross. Blues and grays were commonly used to portray the color of dead flesh. Ribs, tendons, and sinews could often be seen stretched through the skin to depict the amount of starvation and agony that Christ endured while on the cross. Jesus's head, once held high now drooped and the dejected body sagged limp from the cross pulling his arms past a 90° angle. These attributes showed the death, suffering, and humanity of Jesus rather than glorifying Christ as the Romanesque period depictions had.¹⁸

Knowing these characteristics, I was able to examine and analyze the diagnostic Romanesque and Gothic characteristics of *Christ*. Visual examination of *Christ* reveals both Romanesque and Gothic characteristics, therefore indicating that it could possibly have originated from a time bridging the Romanesque and Gothic Periods in which both styles were still in use. For example, the torso of the figure is twisted, the head is drooped, the arms are pulled past 90°, and the rib cage is exposed. All of these indicate that the sculpture was created during the Gothic period. The feet of the figure, however, are separated and four nails were used. Furthermore,

chemical analysis revealed that the believed original pigment layers were pinks and flesh tones. The use of four nails and live flesh tones is characteristic of the Romanesque period of Medieval art.

Despite a few remaining uncertainties about this piece, this interdisciplinary approach has offered much insight into the creation and chronology of *Christ*. I chose to take on this thesis research through an interdisciplinary approach because it was the perfect fit for my set of majors. I am a double major in Chemistry and Archaeology with a minor in History. I hope to pursue a career as an archaeochemist within a museum lab and to unlock the mysteries of other artifacts through chemical analysis. The chemical techniques and archival research skills obtained through this research with not only directly contributed to my fields of study, but also to added to my overall knowledge toolkit. I am proud to say that my independent research will also contribute to the David Owsley Museum's knowledge of the *Christ* sculpture.

Completing work on thesis has taught me more than just chemical analysis techniques and historical trivia. This thesis has highlighted the importance of interdisciplinary work. I have always valued gaining multiple perspectives and approaching problems from multiple fields of study. I believe that it is this interdisciplinary collaboration that not only helps advance knowledge in individual fields, but makes that knowledge readily available to the masses. For this reason, I am and always will be an advocate for interdisciplinary research, especially during the formative years of undergraduate study. Students need to specialize and generalize their education at the same time. They need to become experts in their field while maintaining a working knowledge of other fields. Most importantly, individuals should always strive to expand their knowledge toolkits, just as the archaeochemical analysis of *Christ* has done for me.

ABSTRACT

An infrared (IR) and scanning electron microscope energy dispersive spectroscopic (SEM-EDS) study of pigments, binders, and grounds removed from a 13th century Medieval sculpture depicting the crucifixion of Christ, which is housed in the David Owsley Museum of Art, was completed. Approximately twenty 4.00 μm samples were analyzed using transmission mode of the Perkin Elmer 100 infrared spectrometer, SEM-EDS, and close microscopic analysis. The original pigment layer is consistent with the 1225-1250 dating of *Christ 1225*. Spectra were compared with reference spectra from the 1994 Artist and Artisans Materials, Infrared Spectral Library and independently obtained reference spectra. The second layer of pigments is consistent with a renovation, likely post 1824. Pigments and compounds identified include lead carbonate, calcium carbonate, kaolinite, ultramarine (likely natural), egg yolk, unknown protein, gypsum, and unknown red pigments. The base is likely oak sculpture in the round.

Keywords: Infrared Spectroscopy, Scanning Electron Microscope – Energy Dispersive Spectroscopy, Medieval, Sculpture-in-the-Round, Pigment analysis

INTRODUCTION

Purpose

The purpose of this research is to utilize moderately-destructive analytical techniques, infrared spectroscopy (IR), Scanning Electron Microscope – Energy Dispersive Spectroscopy (SEM-EDS), and close microscopic analysis to gain a comprehensive understanding of the elemental and molecular composition of the pigments, binders, and other materials removed from the medieval crucifix titled *Christ* housed at the David Owsley Museum of Art. Through connection of the material analysis to known historical periods, this analysis seeks to determine if the 1225-1250 dating of the sculpture is consistent with the materials used, create a

hypothetical chronology of the crucifix, and to provide information for future conservation and preservation of the piece.

Many analytical techniques are available for the elucidation and characterization of chemical molecular and elemental structures of paints used on archaeological and artistic artifacts. Some such techniques include laser-induced breakdown spectroscopy, UV-visible absorption, nuclear magnetic resonance spectroscopy, x-ray diffraction, x-ray fluorescence, and energy dispersive X-ray spectroscopy. In order to preserve the cultural and historical integrity of a piece, however, it is important to use the least destructive analytical techniques available for identification of pigments. For this reason, Fourier Transform IR spectroscopy, SEM-EDS, and close microscopic examination were the techniques chosen to analyze samples taken from *Christ*. These analysis methods provide complementary molecular and atomic information.

These techniques also maintain the integrity of the piece because they require small samples on the order of 250-750 μm in diameter. Samples were removed from previously deteriorated and inconspicuous locations on the sculpture to avoid any visibly discernable damage to the piece. Furthermore, FT-IR and SEM-EDS do not require the permanent destruction of the sample, therefore each sample could be analyzed several times before any additional sampling or movement of sculpture was required. Close microscopic analysis of the samples using a stereomicroscope also allowed for physical separation of layers when present to obtain relatively pure samples from a mixed medium.

Infrared Spectroscopy, useful in determining molecular composition, was the primary technique utilized in this analysis. SEM-EDS was used to confirm or supplement the results determined by the infrared spectral data and provided information on inorganic and metallic substances present.

Understanding the Sculpture

Christ is a painted wooden polychrome sculpture currently housed at the David Owsley Museum of Art on the campus of Ball State University in Muncie, Indiana. According to the Ball State University Libraries' Digital Media Repository *Christ*, dating from 1225-1250, was acquired by the museum in 1991 through a generous donation from David T. Owsley in memory of his mother Lucy Ball Owsley. This piece, made of wood, metal, and paint, is believed to have been created by an unknown Spanish artist in the Northern Catalan region of Spain. This sculpture measures approximately 174 cm by 191 cm by 40 cm and is mounted on a wall with a single wire and wooden support block.¹ *Christ*, as he is displayed at the David Owsley Museum of Art, can be seen in Figure 1.

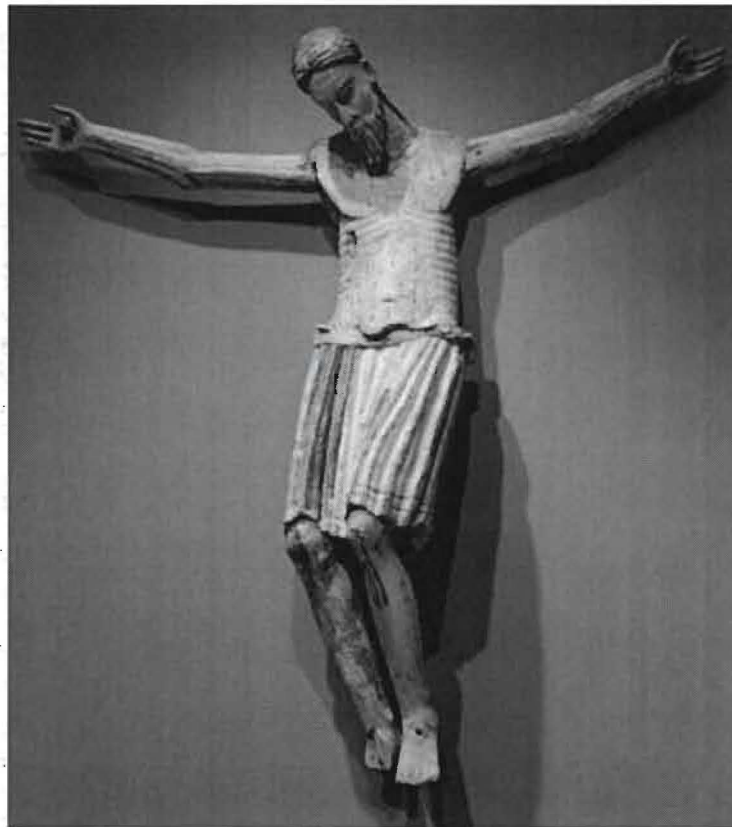


Figure 1: Christ on Display at the David Owsley Museum of Art

EXPERIMENT/METHODS

Sampling

Composition analysis of the Spanish Crucifix began with visual analysis of the paint layers. Utilizing a ultra-violet light the sculpture's layers were analyzed for fluorescence and ultra-violet active materials. Material analysis involved carefully removing paint samples of approximately 250-750 μm in diameter from inconspicuous areas on the sculpture. In order to minimize damage to the artifact, samples were removed from already deteriorating areas of the sculpture.

Approximately nineteen unique samples were removed from various areas of the sculpture using a pre-cleaned sharpened scalpel and a needle tipped probe. Each sample was then placed between two pre-cleaned microscope slides, sealed in with Scotch tape, and labeled with a sample number and location from which the sample was taken. The microscope scraped clean with razor blades and progressively washed with concentrated acetone and millipore purified water.

Nineteen different samples were obtained from different locations on the sculpture over three visits to the museum. Samples were acquired over a period from March 38, 2014 through September 25, 2014.

Sample Analysis

Each sample was visually analyzed using a stereomicroscope. The colors, particle size, layers, homogeneity of particle size and mixtures, and the layers present in each sample were noted. Theoretical layers of each sample were then drawn noting the relative depth, color, and location of each layer.

Samples were then analyzed using a Perkin-Elmer Spectrum 100 infrared spectrometer with a 4.00 cm^{-1} resolution. Most spectra were run with a scan number of 16 in order to reduce

the baseline noise. Using an Attenuated Total Reflectance (ATR) with a diamond crystal 7 μ m in diameter, each scan was performed with a strong apodization, a magnitude phase correction, a scan speed of 0.20 cm/s, and a CO₂/H₂O correction. Analyses were performed with Spectrum software.

In order to perform each scan, first a blank was run using only the diamond crystal cleaned with methanol in order to calibrate the spectrometer. Each paint sample was then placed on the stainless steel plate surrounding the crystal and slid across the plate onto the diamond crystal with an acetone cleaned microspatula and needle probe. This process was repeated for each color from each sample multiple times in order to determine reproducible data.

Each spectrum was then closely analyzed for distinctive peak frequencies, relative intensity of absorption bands, and common peak patterns associated with certain functional groups such as amines found in various proteins. This examination process included comparing the sample spectra with reference spectra available in the July 1993 Infrared Spectral Library, Artist and Artisan Materials.² Conclusions were also referenced with known time periods of use for certain pigments found in Chemistry and Artists' Colors, Second Edition.³

Several paint samples thought to contain some metallic elements were further analyzed using X-ray spectrometry. This analysis helped determine the presence and relative amounts of elements present in some of the samples. To do this, 0.5 to 1.0 millimeter fragments of pigment were cut away from larger samples under a microscope and were adhered to carbon tabs. These tabs were then placed on a scanning electron microscope stage and spectral data was obtained.

Samples requiring further SEM-EDS analysis were sent to labs at the Miami University. Quality of some SEM images were compromised due to extreme charging effects in some of the samples. EDS spectra were obtained at 30 keV for 200 laser seconds. Carbon and oxygen were

included in the breakdown of the elemental analysis when calculating weight percent and atomic percent.

RESULTS

After examination, the overall stratigraphy of the paint strata on the sculpture breaks down into four primary layers consisting of two layers of ground and two mixed pigment and binder layers. The first pigment layer and first ground directly adjacent to the wood are believed to be the original layers. The presence of a second ground and pigment layer with different compositions than those of the original pigment and ground layers is indicative of a renovation of the piece.

Analysis of layers was performed through categorization of sampling areas and then by color. The four primary sampling areas include the left ankle, the navel, the skirt, and the right calf and shin of the Christ figure.

Ground Layer One: Seems to be the Original Ground Layer

The first ground layer to be definitively identified appears to be the original ground layer. This layer is closest to the wood base and was observed in multiple spectra from various samples. The spectrum shown in Figure 2 matches the infrared spectrum for gypsum found in the RRUFF Database of Spectroscopy.⁴ Spectra of the underside of Sample 0, believed to be the original ground layer, taken from the dark gray and black region in the mid-outside of the right calf. Distinctive peaks for gypsum in this spectrum lie around 3525 cm^{-1} , 3400 cm^{-1} , 1685 cm^{-1} , 1620 cm^{-1} , 660 cm^{-1} , 600 cm^{-1} . Gypsum peaks were present on all spectra from the white underside of original layer samples – all samples excluding Sample 16.

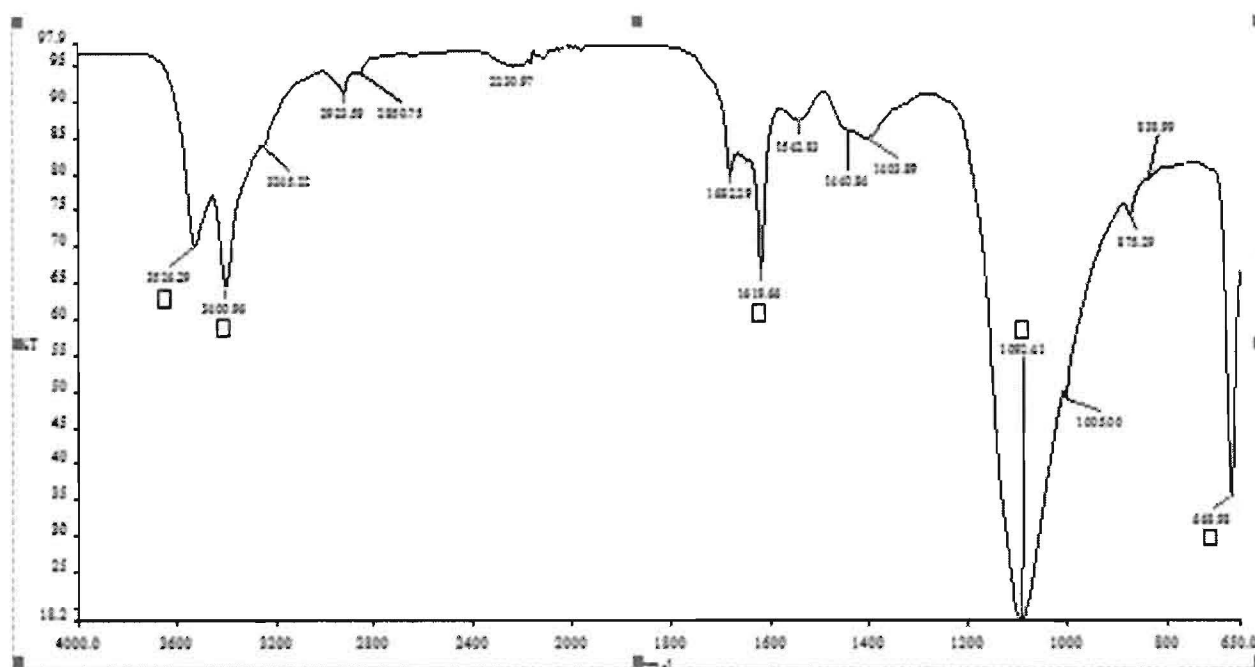


Figure 2: Underside of Sample 0 showing the cleanest spectrum of the original ground layer

Spectral peaks indicative of an unknown protein also occurred in this layer as evidenced in several spectra of the white underside of the first pigment layer. The absence of an ester peak around 1725 cm^{-1} indicates that the protein is not an egg yolk. This protein is not an egg yolk. The lack of an ester leaves the possibility of an egg white, animal glue, or oil as a protein binder. All of these were commonly used binders during the medieval times.⁵

Pigment Layer One: Seems to be the Original Pigment Layer

Ankle: Pink Pigment

Sample 14 was also removed from the lower pink layer on the bend of the left foot leading into the leg. A spectrum of the white underside of this chip was obtained in order to confirm that sample 14 is part of the original pigment layer. This spectrum was nearly pure gypsum indicating that it was part of the first ground layer, therefore confirming that sample 14 is representative of the light pink flesh color within the original pigment layer. This layer also

contains an unknown protein and an unknown pink pigment (likely ultramarine red). This spectrum can be seen in Figure 3.

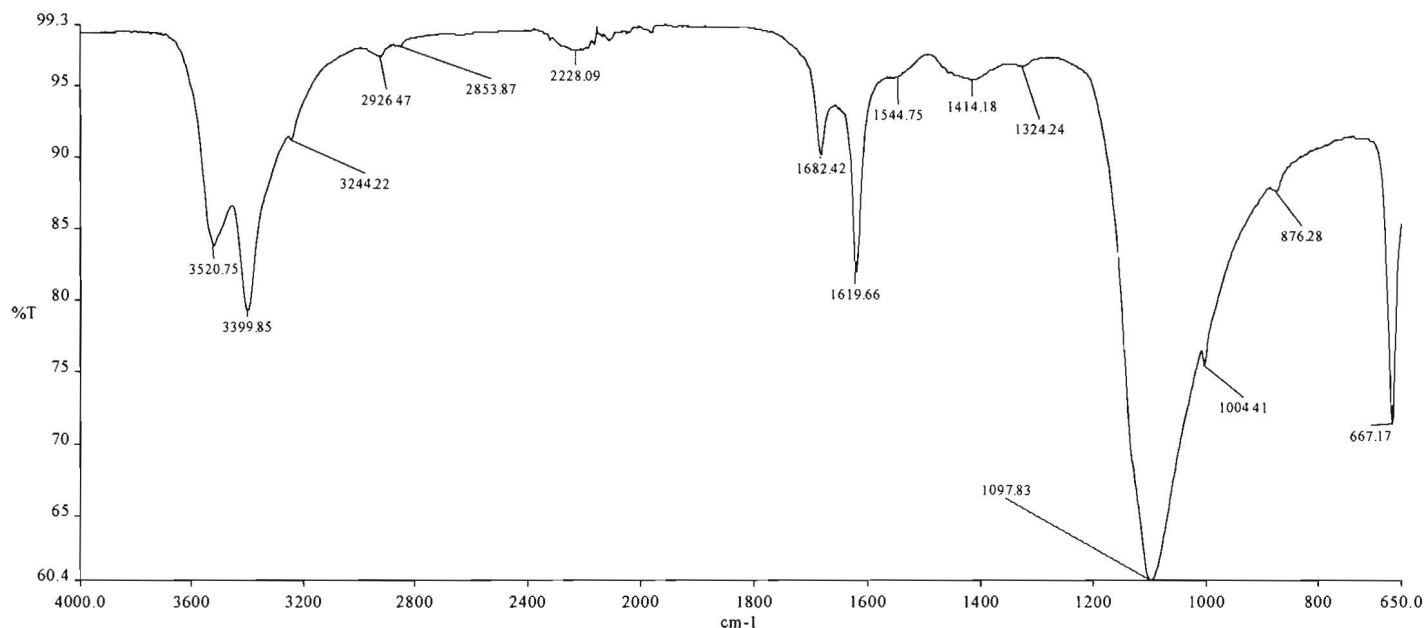


Figure 3: Underside of Sample 14 indicating a nearly pure gypsum (original) ground

Belly Button: Pink Pigment

Sample 4 was taken from the lower pink layer left of the belly button. Spectra of this sample, seen in Figure 4, had characteristic gypsum peaks 3530.53 cm^{-1} , 3400.70 cm^{-1} , 1619.78 cm^{-1} , 1103.46 cm^{-1} , and 676.92 cm^{-1} . The infrared spectrum of the white underside of this sample is almost pure gypsum. This layer was initially believed to be the same pigment as that of sample twelve. Sample 4 also contained egg yolk protein, and unknown red pigment. The x-ray spectra of sample 4 displayed large amounts of lead and trace amounts of sodium, oxygen, and

aluminum. The most intense lead peak in the spectrum also overlays the location of a potential silicon peak. The lead is likely to be a contamination from the adjacent second ground layer. The presence of key elements such as sodium, aluminum, silicon, and oxygen are characteristic of an ultramarine compound. The molecular formula for ultramarines is $\text{Na}_{8-10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$.

Ultramarine red and ultramarine violet typically contain four sulfurs compared to only two sulfurs in ultramarine blue. Close microscopic examination of red pigment particles within this sample revealed that pigment pieces were largely non-uniform and therefore more likely to have been natural ultramarine, commonly used before 1300, rather than synthetic ultramarine with its first documented use in 1824.³

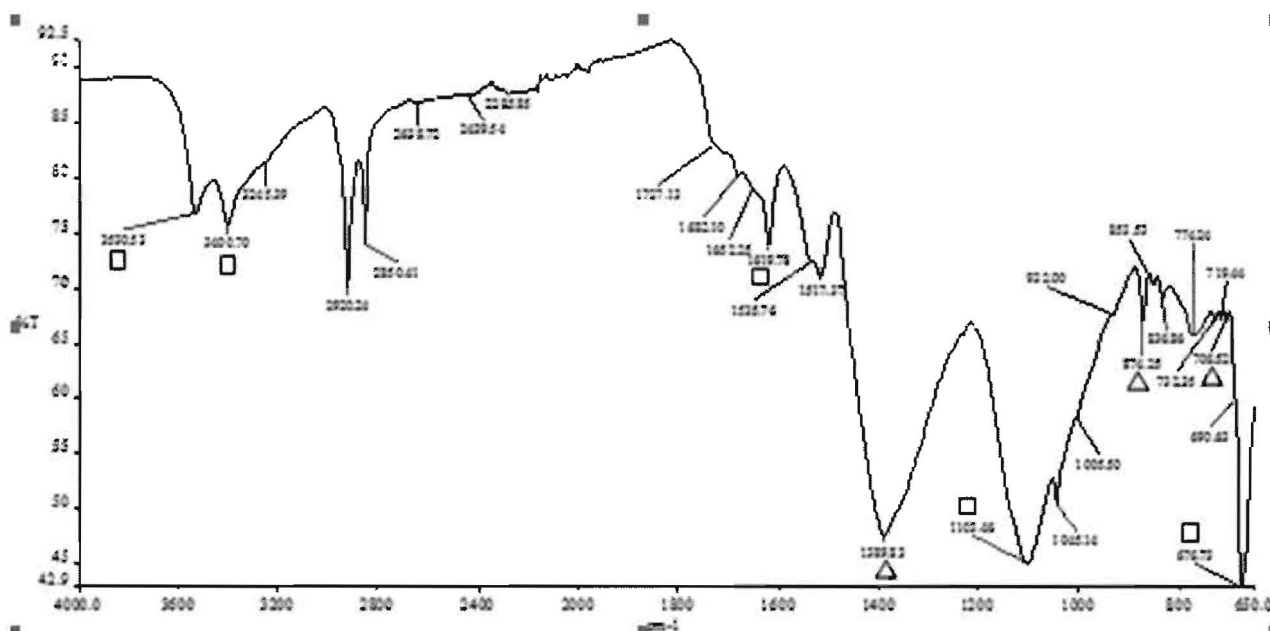


Figure 4: Top of Original Pink Layer of Sample 4 removed from the belly button

Sample 18 was also removed from the pink layer below the second ground to the lower left of the navel. The representative spectra can be seen in Figure 5. Characteristic gypsum, lead carbonate, and egg yolk amide stretches can be seen. Lead carbonate in this spectrum is characteristic of contamination from the adjacent layer. Two particular peaks of interest occur at 1142.32 cm^{-1} and 1033.57 cm^{-1} . These may indicate the presence of clays or an ultramarine red.

Although spectra of this sample are similar to those of sample 4, results from this sample are inconclusive, however, due to the inability to replicate spectra with the limited amount of sample.

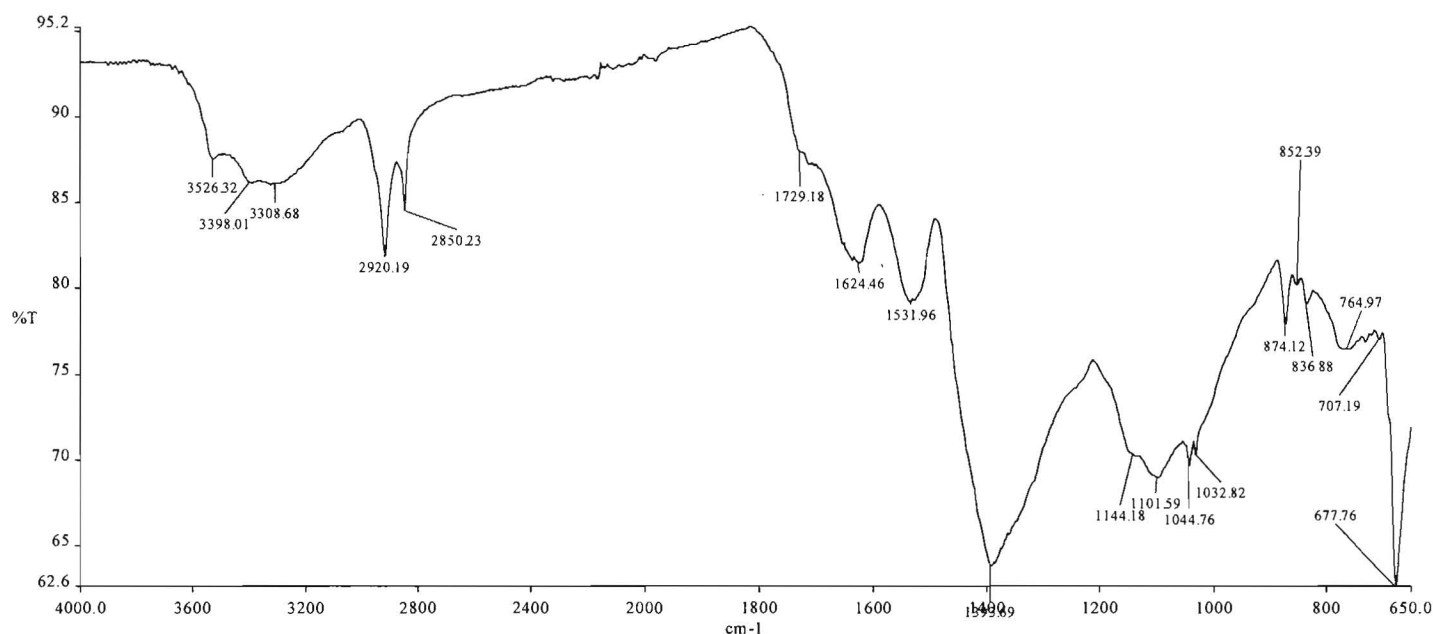


Figure 5: Pink Pigment in Sample 18

Skirt: Orange/Brown Pigment

Sample 7, taken from the original orange-brown pigment layer on the skirt, was found to contain kaolinite. Kaolinite peaks in the sample infrared spectrum were compared with reference spectrum in The Coblentz Society Desk Book of Infrared Spectra.⁶ Distinctive kaolinite peaks were observed at 3696.85 cm⁻¹, 3621.31 cm⁻¹, 1098.33 cm⁻¹, 1034.74 cm⁻¹, 1004.08 cm⁻¹, 911.79 cm⁻¹, 828.46 cm⁻¹, 795.10 cm⁻¹, and 751.27 cm⁻¹ as seen in Figure 6. The presence of several gypsum peaks indicates that this layer is between the two layers of ground, thus confirming that it is part of the first pigment layer. Additional SEM-EDS analysis, represented in Figure 7, was performed on this sample. The presence of iron and oxygen were identified. This is indicative of iron oxides that contribute to the red-orange color found in iron rich soils. The presence of iron oxides in addition to a large silicon peak in the X-ray spectra, confirms the presence of clay or

soil in the sample. The infrared spectra of this sample also contained several characteristic gypsum peaks which indicates that it was directly adjacent to the first ground and part of the original pigment layer.

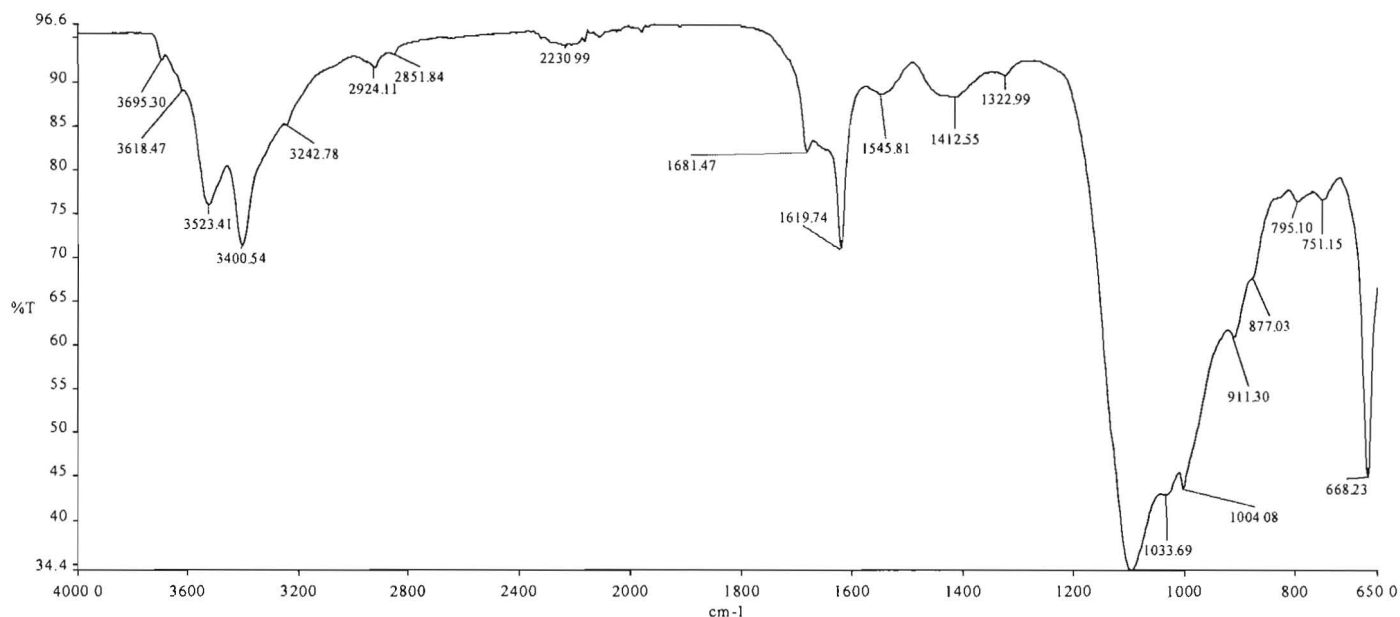


Figure 6: Red/Orange Original Pigment Layer in Sample 7

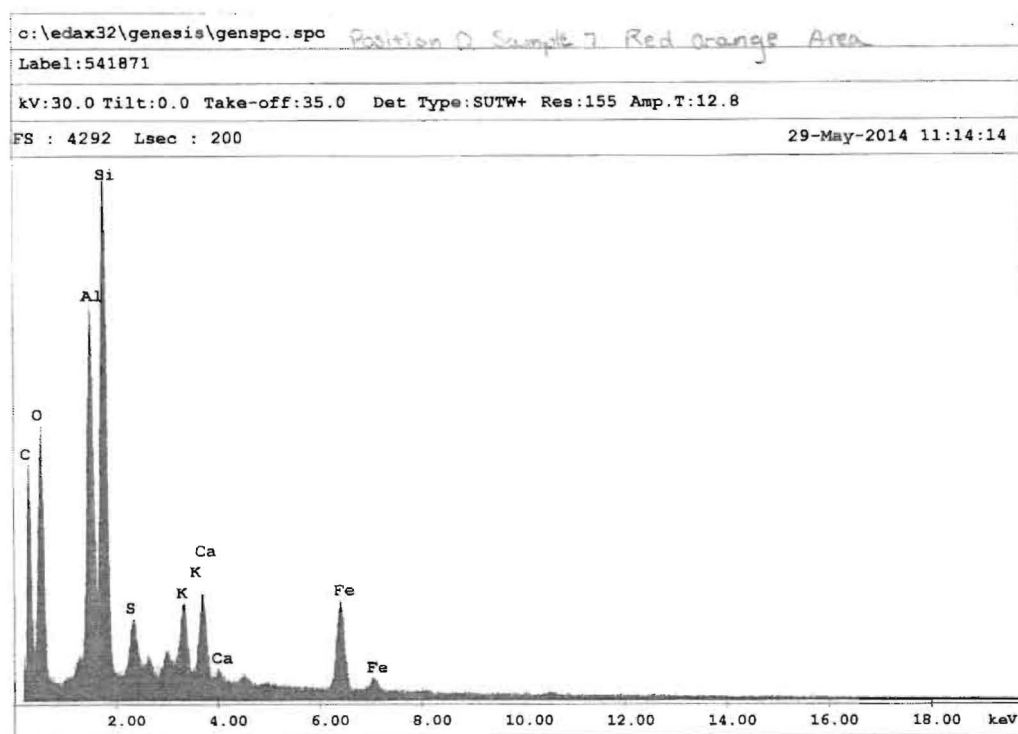


Figure 7: SEM-EDS Spectrum of Sample 7 Original Pigment Layer

Ground Layer Two

The second ground layer was applied over the first layer of pigment at a later time. The composition of this layer is primarily lead carbonate. Weak infrared peaks appearing around 1400 cm^{-1} , 875 cm^{-1} , and 705 cm^{-1} indicate the presence of a carbonate. These peaks are believed to correspond to lead(II) carbonate which was found in several red, blue, and other colored samples from the second pigment layer. This compound was first identified as lead (II) carbonate using reference spectrum obtained using the same infrared spectrometer and a reagent grade lead(II) carbonate from Fisher Chemical. Distinctive lead (II) carbonate peaks were observed at 670.00 cm^{-1} , 1044.86 cm^{-1} , 1392.55 cm^{-1} , 1737.04 cm^{-1} , and 3568.15 cm^{-1} . Additional SEM-EDS spectral analysis was performed. The presence of lead in the SEM-EDS spectrum confirmed the presence of lead carbonate in several of the pigment samples. Lead white was commonly used before 1300 as a whitener or extender.⁷ The presence of lead throughout many of the pigment samples and as the primary component of the second ground layer indicate that it may have been used as a ground, a whitener, and an extender in the production and subsequent renovations of this piece.

Pigment Layer Two

A protein binder was observed in several samples from various regions in on the sculpture. This protein was identified as egg yolk through comparison with reference spectrum found in Artist and Artisans Materials, Infrared Spectral Library.² Some characteristic peaks of what is believed to be a protein in egg yolks can be seen in spectra 4.3.14.pp15.6 of Sample 0. These peaks occur at 3251.38 cm^{-1} , 2920.37 cm^{-1} , 2850.88 cm^{-1} , 1724.19 cm^{-1} , 1640.27 cm^{-1} , and 1537.16 cm^{-1} . Microscopic observation of shiny deep goldenrod flecks present throughout many of the pigment samples also indicated the potential presence of egg yolk.

Ankle: Pink Layer

Sample 12 was removed from both the upper and lower pink layers on the inside of the left ankle. Examination of stratigraphy under a microscope indicated that the top layer of the sample was part of the second pigment stratum. Infrared analysis, represented in Figure 8, of this layer indicated the presence of gypsum, lead carbonate, calcium carbonate, a protein binder (egg yolk), and an unknown red pigment. The gypsum is likely contamination from an adjacent layer. X-ray analysis of this sample denoted the presence of mercury and sulfur, as seen in Figure 9. Mercury and sulfur are the two elements that comprise mercury (II) sulfide. Use of mercury sulfide, commonly referred to as cinnabar, is documented prior to 1300.² Given the presence of both calcium carbonate and lead carbonate in the same sample layer as cinnabar, it is likely that HgS is part of the second pigment layer. Re-sampling of this portion is required to confirm this conclusion.

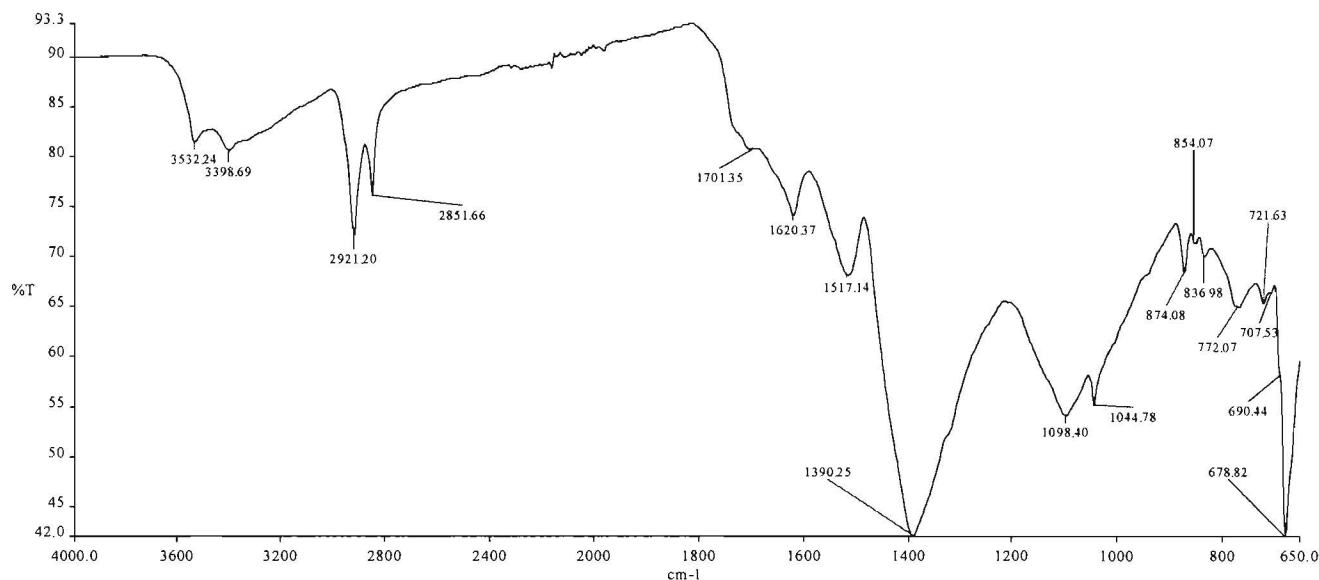


Figure 8: Infrared Spectrum of Upper Pink Layer of Sample 12 removed from the left ankle

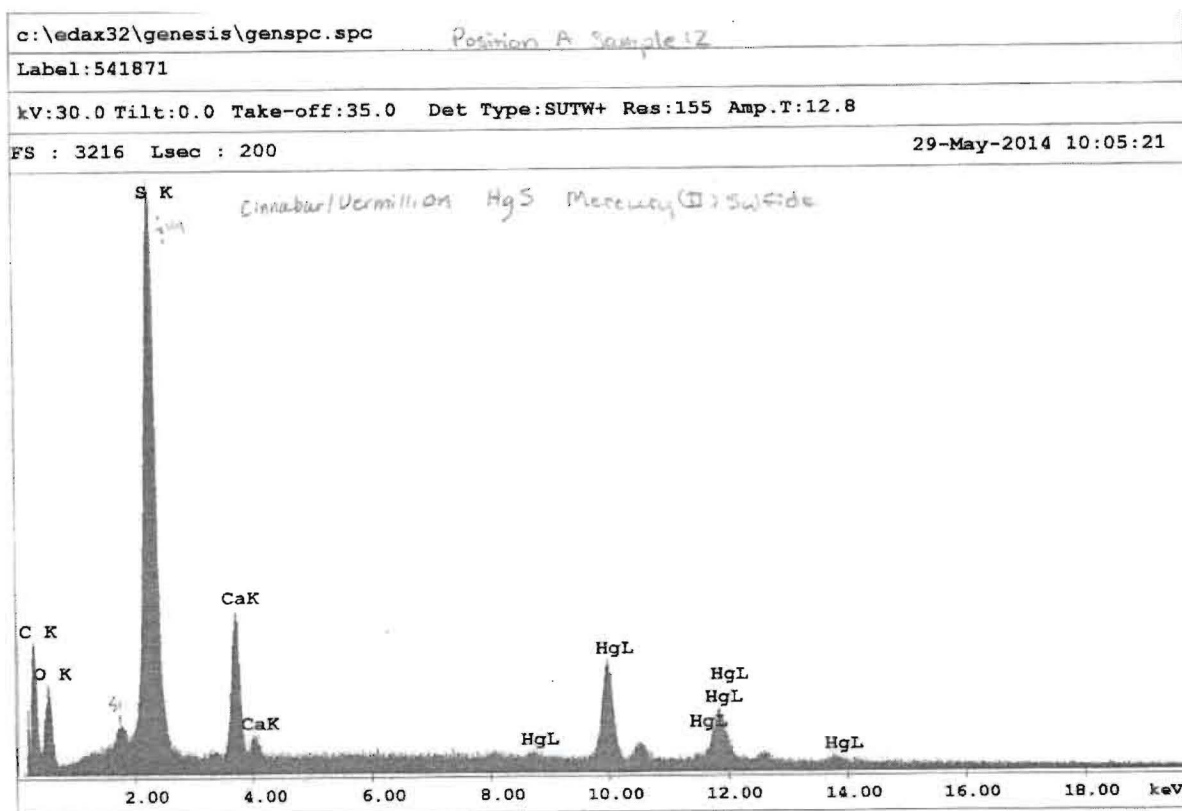


Figure 9: SEM-EDS Spectrum of Sample 12 removed from the left ankle

Navel: Blue Pigment

Sample 2 was removed from the top blue layer on the top right of the navel. According to close microscopic analysis, this chip is likely to contain both the original and the second ground and pigment layers. The white underside of this multi-layer sample is likely the original ground layer, while the top of the chip is the second pigment layer. The original pigment layer and the second ground layer are sandwiched between these two layers. Infrared spectra of the bottom most white layer indicates primarily gypsum suggesting that this is the original ground layer. Microscopic examination of sample 2, however, indicates that the chip contained multiple layers. The blue gray pigment is part of the top layer. Infrared spectra of the blue gray layer, represented by Figure 10, were compared with spectra found in the 1994 Artist and Artisans Materials, Infrared Spectral Library. Reference spectra 526 of natural Lapis Lazuli Ultramarine

and 532 have intense peaks between 1000 cm^{-1} and 1110 cm^{-1} , small thin peaks near 2850 cm^{-1} , 2920 cm^{-1} , and a broad peak around 3400 cm^{-1} .² The infrared spectra of the top blue layer, believed to be the second pigment layer, of sample 2 has peaks corresponding to all of the peaks found in the reference for ultramarine blue. Peaks for lead carbonate occur around the same wave numbers and therefore may obstruct the presence of small amounts of ultramarine blue present. A protein with an ester peak around 1726 cm^{-1} is also present. This is typical of egg yolk, which is consistent with proteins seen in previous sample spectra from the second ground and second pigment layers. Calcium carbonate is also present as evidenced by the peak around 872.40 cm^{-1} . SEM-EDS analysis has a stair step pattern near 1.5 to 2.0 keV. This same pattern, indicative of sodium, aluminum, and sulfur can be seen in the x-ray spectrum of sample 0 and is indicative of a mineral based pigment such as ultramarine blue. Several other elements including calcium, carbon, oxygen, and lead appear in the x-ray spectrum which is typical of lead carbonate and calcium carbonate.

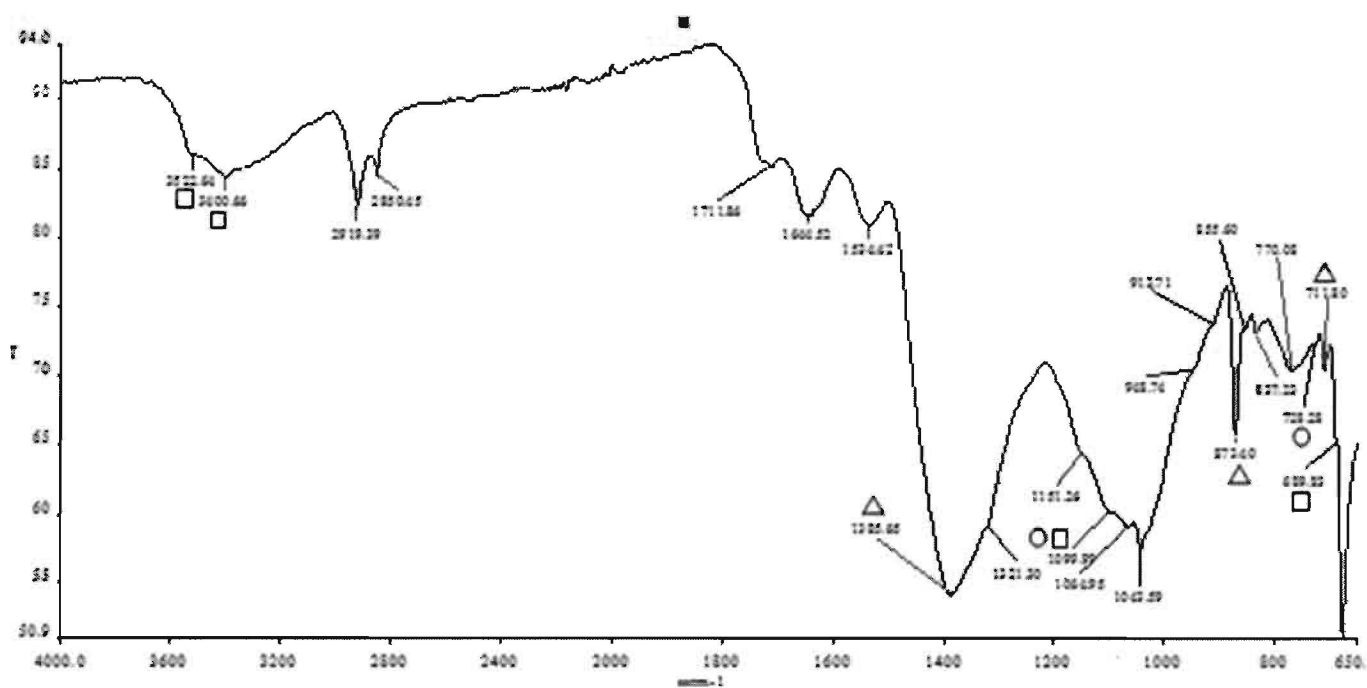


Figure 10: Infrared Spectrum of Top Gray/Blue Layer of Sample 2 removed from the belly button

Skirt: White Pigment

Sample 6 was also removed from the top white layer of the skirt. A thin wispy adhesive like gray layer was removed from the underside of the white paint chip removed. Infrared spectra, represented by Figure 11, of the white layer indicated trace amounts of an egg yolk protein and large amounts of lead carbonate and calcium carbonate. Very minor amounts of gypsum were present in the sample. This is due to cross contamination between layers. The most recent white pigment layer on the skirt is primarily calcium carbonate and lead carbonate mixed with egg yolk.

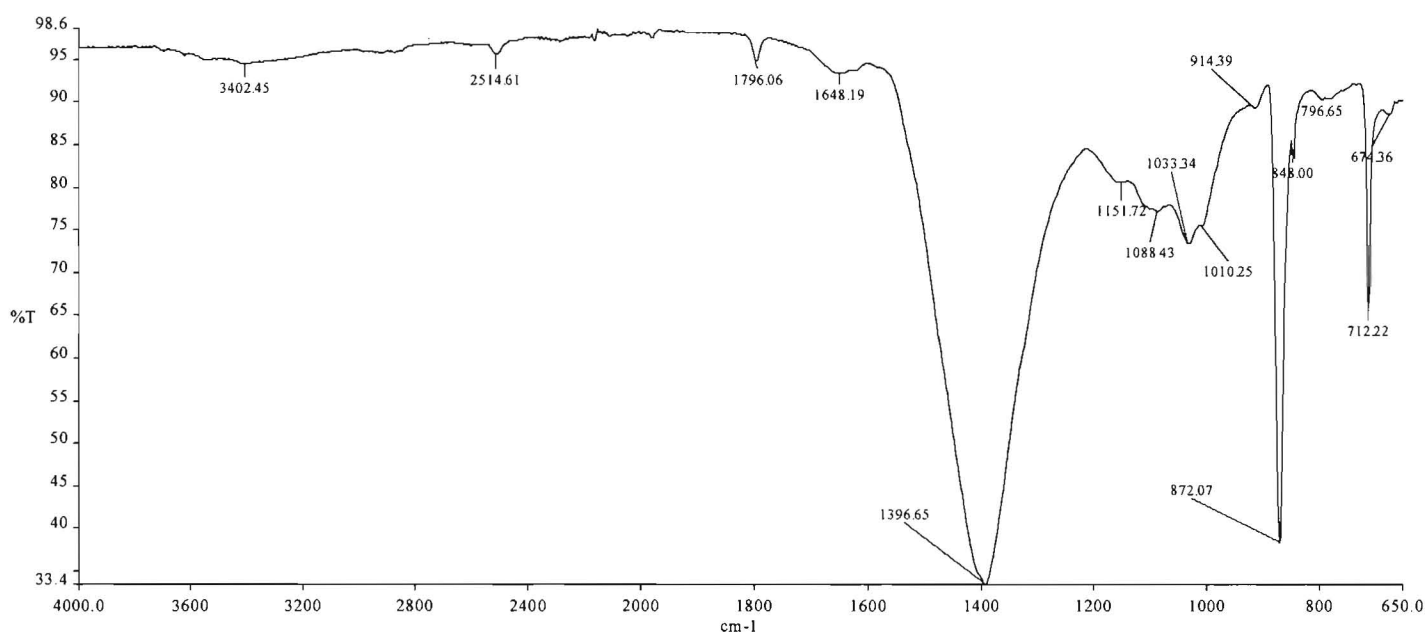


Figure 11: Infrared Spectrum of the White Pigment from the top layer of the skirt

Skirt: Blue Pigment

Sample 8 was taken from the lower blue stripe from the top layer located at the bottom of the skirt. Infrared spectra for this stripe show distinctive peaks for lead carbonate and calcium carbonate around 1396.94 cm^{-1} and 872.04 cm^{-1} respectively. An ester peak at 1726.83 cm^{-1} is indicative of the egg yolk binder present in the top two layers. An ultramarine peak occurs at 1108.99 cm^{-1} . Ultramarine peaks also occur at 1045.24 cm^{-1} , 907.39 cm^{-1} , 768.38 cm^{-1} , and

690.49 cm^{-1} . These can be seen in Figure 12. The presence of large amounts of lead carbonate obstructed additional ultramarine peaks in several spectra of this sample. SEM-EDS spectra confirmed the presence of lead carbonate.

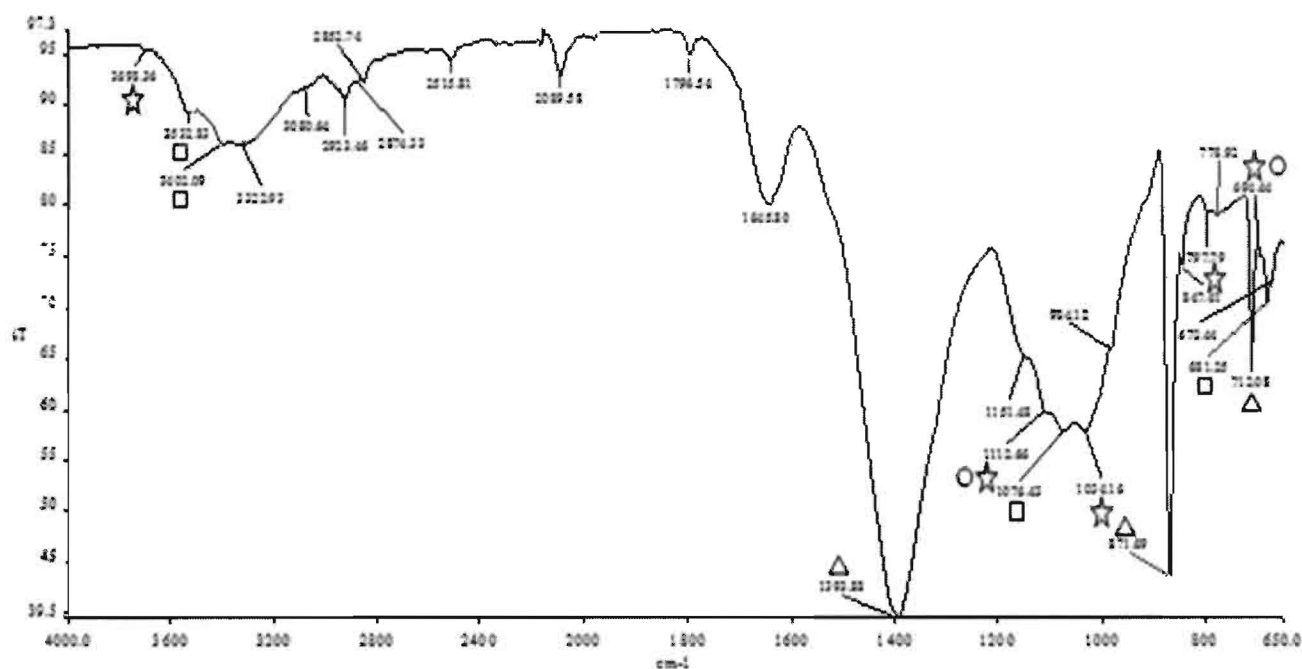


Figure 12: Infrared Spectrum of the teal strip from the bottom of the skirt

Sample 19 was also taken from the teal stripe of the skirt. IR spectra of the top layer confirmed the top teal stripe layer composition to be an egg yolk binder mixed with lead carbonate, calcium carbonate, and ultramarine blue. Close microscopic analysis of the sample revealed non-uniform size and shape particles which is representative of natural ultramarine. The first documented manufacture and use of synthetic ultramarine was 1824, therefore it is likely that the renovation of this piece occurred before 1824.³

Calf/Shin: Dark Gray/Black/Brown Pigment

Sample 0, taken from the dark gray and black pigment layer located on the outside right calf of the figure contained an inorganic pigment mixed with an egg yolk protein binder, gypsum, lead carbonate, calcium carbonate, and an unknown clay based silicate. Infrared spectra of the

white underside of this sample indicate primarily gypsum with trace amounts of calcium carbonate suggesting that this is part of the original pigment layer just above the original gypsum ground. Microscopic examination of sample 0, however, indicates that the chip contained multiple layers ranging from the original layer to the top pigment layer. An infrared spectrum of what is believed to be the top pigment layer can be seen in Figure 13. The gray black pigment layer appears to be the top layer according to stratigraphic analysis. Spectrum 4.3.14.pp15.6 seen below has peaks around 3251.38 cm^{-1} , 2920.37 cm^{-1} , 2850.88 cm^{-1} , 1724.19 cm^{-1} , 1640.27 cm^{-1} , and 1537.16 cm^{-1} . These peaks correspond to a protein signature found in egg yolk. Infrared identification of the lead carbonate and calcium carbonate is supported by x-ray spectral analysis which indicates the presence of several elements including calcium, carbon, and oxygen typical of calcium carbonate; sodium, aluminum, and silicon typical of a clay based silicate; and large amounts of lead indicative of a lead carbonate. The pigment is undetermined, however, infrared spectra of this sample are very similar to spectra of sample 2, which was taken from the top pigment layer near the belly button. Lead white turns dark gray or black after long term exposure to air, water, and degradative oils which may be one explanation why this layer appears visually different, despite having similar spectra to those of sample 2. An additional explanation is provided in the discussion section.

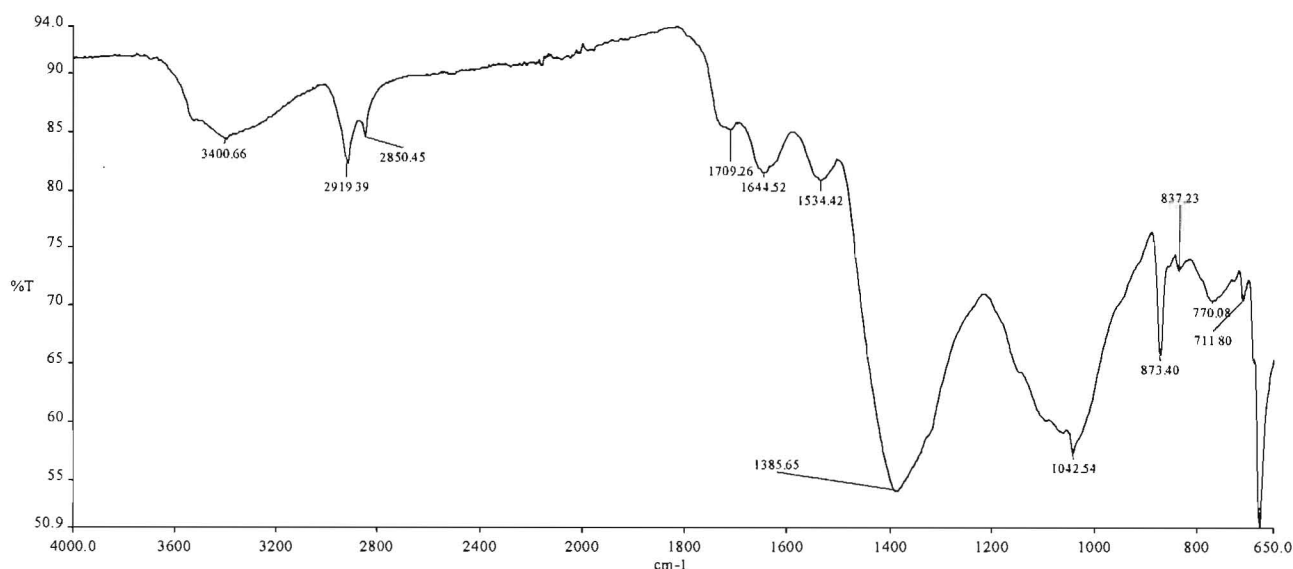


Figure 13: Infrared Spectrum of the Top Dark Gray layer removed from the right calf

Sample 17 was exhumed from the right leg just under the front of the knee. This chip included all ground and pigment layers present. Spectra of the bottom layer of this chip indicated primarily gypsum, confirming that it is part of the first ground layer. The top black brown layer was also analyzed. Spectra of this layer, represented in Figure 14, indicated lead carbonate, calcium carbonate, an egg yolk binder, and an unknown pigment. Gypsum from an adjacent layer was also present within spectra of this sample due to the combination of layers when the sample was crushed against the diamond crystal.

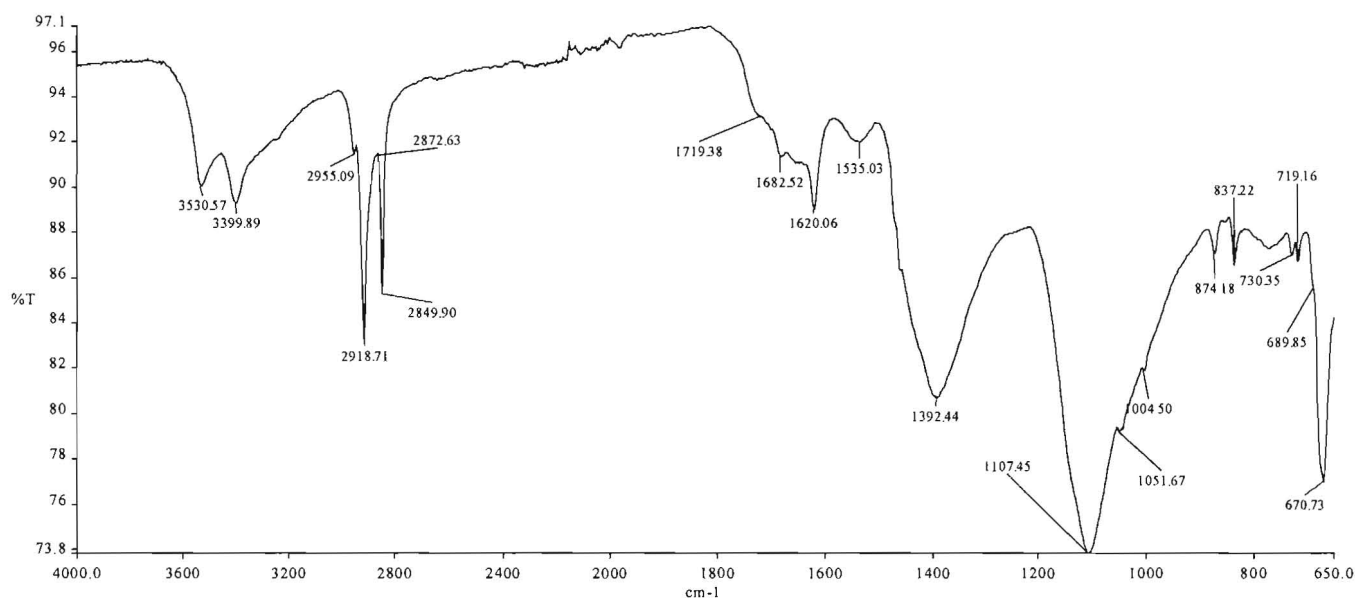


Figure 14: Infrared Spectrum from the Second Pigment and Ground Layers removed from the right calf

Sample 10 was taken from the upper-middle region of the right shin of the figure. Infrared spectra of this sample, seen in Figure 15, showed characteristic gypsum peaks at 3534.86 cm^{-1} , 3400.25 cm^{-1} , 1621.73 cm^{-1} , 1099.09 cm^{-1} , and 675.86 cm^{-1} . Characteristic lead carbonate peaks were displayed at 1383.19 cm^{-1} and 705.62 cm^{-1} . Characteristic calcium carbonate peaks were displayed at 874.54 cm^{-1} . A translucent glaze was observed on this sample and is believed to contribute to the protein peaks found throughout the infrared spectra. As with previous samples, the glaze is believed to be comprised of egg yolk. In order see the greatest

amount of stratigraphy this sample was cut through all pigment and ground layers all the way down to the wooden base of the sculpture. As predicted the white underside of this crosscut was the very first ground layer comprised of primarily gypsum. The x-ray spectra of sample 10, represented in Figure 16, displayed lead and trace amounts of sodium, calcium, oxygen, carbon, iron, and aluminum. The presence of several of these key elements is characteristic of a mineral based red pigment. Conclusive identification of the red pigment was not determined, however, due to the inability to re-sample and re-run x-ray analysis on similar pigment samples.

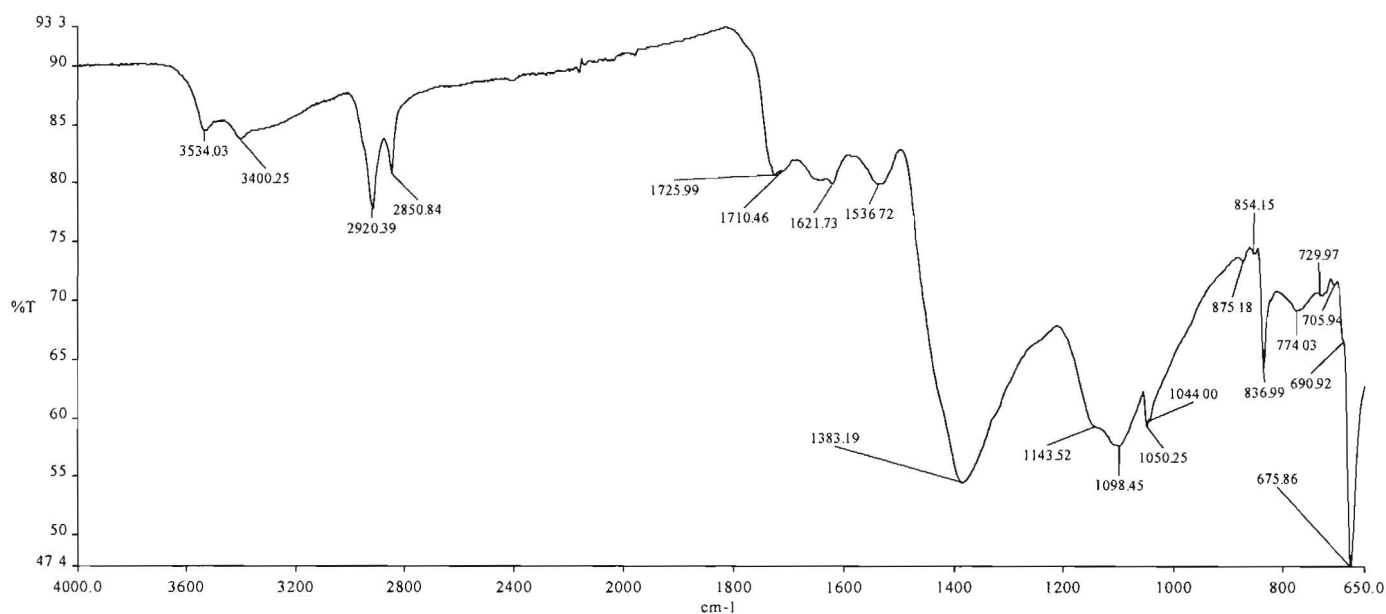


Figure 15: Infrared Spectrum of the Top Pigment Layer of Sample 10

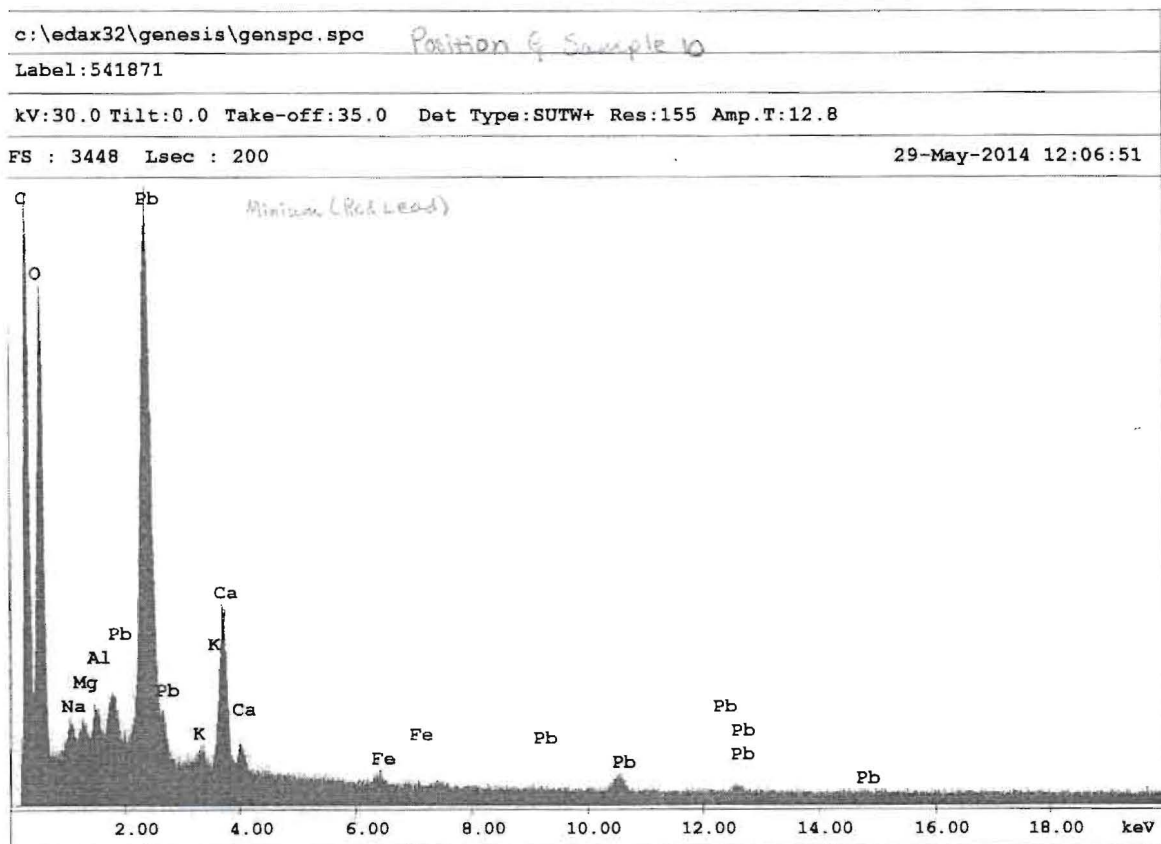


Figure 16: SEM-EDS Spectrum of Sample 10

Hip: Mixed Pigment

Sample 1 was taken from the right hip of the sculpture just below the tunic belt. This sample contained a mixture of tan colored sand like grains, small even black grains, and large, irregularly shaped shiny red pigment globules. The texture was powdery making it difficult to obtain clean infrared spectra with a flat base line. This spectra reveals intense bands characteristic of gypsum, trace amounts of calcium carbonate, a protein binder (egg yolk), and an unknown red pigment. The SEM-EDS spectrum reveals the presence of carbon, oxygen, aluminum, lead, calcium, iron, and copper. The occurrence of aluminum, iron, and copper all indicate the presence of a soil based pigment. Identification of the unknown red pigment was inconclusive, however, due to the inability to obtain clean spectra from the powdery mixed

sample. The concentration of the pigment within the sample 1 mixture was simply too small to allow for further analysis.

DISCUSSION



Image 1: Photograph of the visual difference between the left and right sides of the Corpus Figure

Analysis of this piece was difficult due to the many layers of pigments and grounds. Analysis was further complicated by a visual difference between the torso and the skirt and legs of the piece. The pigment and ground layers on the torso of the sculpture were consistent with those found on the skirt. The visual difference between the lower half of the sculpture and the torso, however, is striking.

Pigment layer appear to be applied across the torso in a manner that creates a consistent layer. Natural degradation patterns expose consistent stratigraphy in various areas. As is evident in Image 1, however, there appears to be a clear visual difference between the left and right sides of the figure's legs and skirt.

The right side of the skirt visually appears dark orange, brown, and red in color. Infrared and SEM-EDS analysis of this layer confirmed that it was part of the original layer. The left side of the skirt visually appears as a white layer with teal decorations. Infrared and SEM-EDS analysis of this layers confirmed that it was part of the second pigment layer. While this chemical stratigraphy seems consistent with that of the torso, the straight line separation of these

two regions between the fourth and fifth ripple from the left of the skirt is unusual. A straight line is atypical of natural degradation patterns indicating human action in the formation of this pattern.

The visual difference between the right and left legs of the figure also indicates human action. Top pigment layers on the right leg of the figure are visually a dark black and gray cracked layer of pigment. The top pigment layer of the left leg, however, appears to be a smooth and pink flesh toned in color. While the right leg is cracked, it does not appear to have ever had a pink layer applied over it as is evident on the left leg. It is possible that the original pigment layers of the sculpture were completely painted over, as is seen on the torso, and then only part of the top ground and pigment layers were removed from the right side of the skirt and legs. It is also possible that only the left side of the sculpture was painted over at some point while the right was left untouched. No literature resources provided such examples of these visual differences. Further stratigraphic and chemical analysis is needed to determine the origin of these unique visual differences.

Energy Dispersive analysis generates a spectrum in which the y-axis represents the number of x-ray signals received from the surface of the sample and the x-axis gives the relative energy level of each count. Peaks are representative of certain elements and compounds. This micro-chemical spectroscopic method is moderately destructive to the artifact when it scans the surface of the pigment samples. Pigment samples were removed from inconspicuous previously degraded areas in order to minimize damage to the piece.

Infrared spectroscopy works by taking advantage of the unique wavelengths at which different functional groups vibrate when hit with infrared light. Small amounts of solid sample

can be ground up with ionic compounds that don't yield an IR reading, allowing the sample to adhere more closely to the diamond plate, thus obtaining a cleaner spectrum. Transmission mode was used during this analysis allowing the use of minute samples. Due to the small sample required, this infrared spectroscopy technique for pigment analysis is unobtrusive and relatively nondestructive to the cultural and historical integrity of the artifact.

Eight compounds were identified including gypsum, lead carbonate, calcium carbonate, ultramarine red, kaolinite, ultramarine blue, mercury sulfide, and egg yolk. All pigments, other than ultramarine blue, are consistent with the sculpture's estimated date, 1225-1250 during the 13th century. The compositions of sampling areas include gypsum and an unknown protein in the first ground layer, natural ultramarine red and unknown protein in the flesh colored first pigment layer, kaolinite and an unknown pigment on the first pigment layer of the skirt, lead carbonate, calcium carbonate, and egg yolk in the second ground layer, natural ultramarine blue and egg yolk in the second pigment layer, and cinnabar blood splatters.

The protein binder is the same in ground one and pigment layer one. All of the pigments within these layers were known to be used throughout Europe before 1300 making them consistent with the medieval time period. If these pigments were applied at the believed time of creation, 1225-1250, it is likely that they are the original layer. The uppermost macroscopic appearance of the sculpture appears to be primarily the second ground and second pigment layer. This may indicate that the original layer is either painted over or absent from other areas of the sculpture.

The original appearance of the figure had pink flesh with a dark brown orange skirt. This was applied over a ground layer of pure gypsum. This is unusual for the time period in which grounds were commonly primarily calcium carbonate. Literature reference, the "Multi-technique

chemical characterization of a 12-13th century painted Crucifix,” has similar findings of a purely gypsum and animal glue ground. The use of gypsum, however, instead of the common medieval artist material calcium carbonate indicates that the artist used a readily available source of gypsum rather than purchasing the common ground calcium carbonate. This could possibly indicate that the artist was a lesser known or unknown artist.

The blue-gray pigment on the flesh of the figure and the stripes on the figure’s skirt appears to be natural ultramarine. Synthetic ultramarine’s first known manufacture and use occurred around 1824.³ Synthetic ultramarine is characterized by small, uniform, and nearly round particles.⁸ Based on close microscopic analysis, the blue crystals in this layer appear to be non-uniform, indicating that it is natural ultramarine. The crystal structure and chemical formula of synthetic and natural ultramarine are very similar, however, the presence of several remaining impurities in natural ultramarine helps to distinguish synthetic from natural ultramarine.⁹ Small amounts of calcium carbonate, the common compound in limestone in which lapis lazuli commonly embeds into the porous texture of, were observed in this layer as shown by the presence of calcium in the SEM-EDS. This further indicates that the ultramarine blue used in the second pigment layer is of natural origin.

The second ground layer and pigment layer primarily consisted of lead carbonate, calcium carbonate, and egg yolk. This pigment was commonly used before 1300 as a ground, white pigment, and a lightener/extender. The widespread usage of this pigment on this piece is consistent with the stated 13th century medieval time period.

One particular pigment of interest was mercury sulfide, commonly referred to as cinnabar. This pigment was observed in SEM-EDS spectra of sample 12, removed from the left ankle of the figure. Cinnabar is a densely packed red crystal that is found in several places

worldwide, although not in large amounts. According to Roman texts, the main source of cinnabar during Roman times was extracted from mines in Sisapo, Spain.¹⁰ Sisapo is known as La Bienvenido today and is located in the southwestern quadrant of Spain. Despite the hypothesis that *Christ 1225* originated from the Catalan region of Spain, it is possible and likely that the cinnabar used came from Spanish mines.

Other materials incorporated into this piece include an oak wood base, metal pegs attaching the head and arms to the torso, and a plant based woven fiber cloth on the skirt. The grain pattern of the wooden base was closely observed under a high power microscope and compared with microscopic images from the “The Mechanical Properties of Wood,”¹¹ and the University of Wisconsin’s Botany 130 *Interactive Glossary for Plant Anatomy*.¹² The wooden oak base was determined to be oak.

REFERENCES

- [1] David Owsley Museum of Art Collection. *Christ*.
<http://libx.bsu.edu/cdm/compoundobject/collection/MuseumBSU/id/1410/rec/2> (accessed Apr. 19, 2015).
- [2] M. Derrick, M. Gergen, Artist and Artisans Materials, Infrared Spectral Library, Infrared Users' Group, 1994.
- [3] M. V. Orna, M. P. Goodstein, Chemistry and Artists' Colors. (1998) 283-284.
- [4] *RRUFF Database*, Downs RT, version 2006; R040029.2 (accessed Apr. 19, 2015).
- [5] Lang, P. L.; Keefer, C. D.; Juenemann, J. C.; Tran, K. V.; Peters, S. M.; Huth, N. M; Joyaux, A. G.; The infrared microspectroscopic and energy dispersive X-ray analysis of paints removed from a painted, medieval sculpture of Saint Wolfgang. *Microchemical Journal* 74, **2003**, 33-46.
- [6] Ed. C. D. Craver, The Coblentz Society desk Book of Infrared Spectra, 2nd ed.
- [7] R.J. Gettens, H. Kühn, W.T. Chase, Lead White, in: A. Roy (Ed.), Artists' Pigments: A Handbook of Their History and Characteristics, vol. 2, National Gallery of Art, Washington, 1993, 67-82.
- [8] Osticiolo, I.; Mendes, N. F. C.; Nevin, A.; Francisco, P.S.C. Gil; Becucci, M.; Castellucci, E.; Analysis of natural and artificial ultramarine blue pigments using laser induced breakdown and pulsed Raman spectroscopy, statistical analysis and light microscopy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **2008**, 1-7.
- [9] J. Plesters, Ultramarine blue, natural and artificial, in: A. Roy (Ed.), Artists' Pigments: A Handbook of Their History and Characteristics, vol. 2, National Gallery of Art, Washington, 1993, 37-66.
- [10] R.J. Gettens, H. Kühn, W.T. Chase, Lead White, in: A. Roy (Ed.), Artists' Pigments: A Handbook of Their History and Characteristics, vol. 2, National Gallery of Art, Washington, 1993, 159-182.
- [11] Record, S. J. *The Mechanical Properties of Wood: Including a Discussion of the Factors Affecting the Mechanical Properties, and Methods of Timber Testing*; J. Wiley & Sons, Inc.: New York, 1914.
- [12] Index of Botany 130: Anatomy Wood. Macerated Oak Wood.
http://botit.botany.wisc.edu/botany_130/anatomy/Wood/Oak_macerated.html (accessed Apr 19, 2015).
- [13] Museum Placard, *Christ*, Accession Number 1991.005.000, David Owsley Museum of Art,

- [14] Web Gallery of Art, The Metropolitan Museum of Art. *Crucifix, 1180-1230*. http://www.wga.hu/html_m/m/master/zunk_sp/zunk_sp3/03crucif.html (accessed Feb. 13, 2014).
- [15] Heilbrunn Timeline of Art History, The Metropolitan Museum of Art. *Crucifix*. <http://www.metmuseum.org/toah/works-of-art/47.100.54> (accessed Feb. 13, 2014).
- [16] Chapuis, J.; "Romanesque Art." *Heilbrunn Timeline of Art History*, New York, The Metropolitan Museum of Art **2000**. http://www.metmuseum.org/toah/hd/rmsq/hd_rmsq.htm (accessed Feb. 13, 2014).
- [17] Fernandes, C. V.; PATHOS-the bodies of Christ on the Cross. Rhetoric of suffering in wooden sculpture found in Portugal. *RIHA Journal* 0078, **2013**.
- [18] Stokstad, M.; A Fourteenth-Century Spanish Wood Carving. *The Bulletin of the Cleveland Museum of Art*, 63, 7, **1976**, 210-222.